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Atmospheric Measurement Techniques Discussions

Interactive comment on "A high volume sampling system for isotope determination of volatile halocarbons and hydrocarbons" *by* E. Bahlmann et al.

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Major comments Referee 1 recommends to add a figure depicting the d13C reproducibility results described in section 3.2.1. As these results only corroborates previously results (Rudolph et al 1997, Redeker, 2007), we find it appropriate to add these data in the supplementary material. A plot showing the range of d13C values observed for each of the organohalogens (section 3.3.2) may indeed be helpful for the reader. We appreciate this suggestion and will add such a figure to the revised manuscript.

Referee 1 has expressed his concerns about the fact that the reproducibility of the

d13C measurements was only tested for the analytical system and requested to justify why this has not been tested for the sampling system. We have to agree to the referee that this omission is some drawback of our work. During the recovery tests the IRMS instrument was out of operation and thus the 13C ratios could not be measured for these experiments. Although we cannot fully rule out this as a source of bias, we have confidence in our d13C measurements. Blanks were checked on a routine base at regular intervals and the blanks contributed less than 0.5% to the overall signal. Thus, we can rule out blank contribution as a significant source of bias. Adsorptive losses or incomplete desorption of the target compounds remain as the most important source of bias during sampling. The kinetic isotope effects for such physical processes are generally small. For instance, adsorption of various aromatic hydrocarbons does not appear to cause significant carbon isotope fractionations (Meckenstock et al., 1999, Harrington et al., 1999; both cited from Goldstein & Law, 2003). Even adsorptive losses of 10% that are associated with a hypothetical kinetic isotope effect of 5‰ would lead to a bias of less than 0.6‰.Ġiven the good recovery rates of our sampling system we still find it sufficient that the reproducibility of the carbon isotope ratio determination was only tested for the analytical system.

A figure as suggested earlier by referee 1 will clearly improve and help to clarify the discussion of d13C measurement (reproducibility vs. concentration). Indeed, six injections of bromomethane and chloromethane were performed at each concentration level between 0.02 and 20 nmole. This will be clarified in the revised manuscript. As pointed out before, blanks were routinely checked and found to be negligible. This will explicitly be stated in the manuscript to clarify this point.

Minor revisions:

The minor revisions are eligible and will be considered for the revision of the manuscript.

p2164, lines 18-19, and p2165, lines 1-2: The sampling was performed within two

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hours with starting times between10 AM and 2 PM. We will clarify this.

P2166, line 6: – The referee is right, this should be behind valve 3. The flow was restricted to 70ml/min. This will be corrected.

P2167, line 12: Indeed, this should be $\frac{3}{4}$ and will be corrected.

P2169, line 14: The desorption occurred at 330°C. This will be corrected in the manuscript.

P2170, line 27: This should be "better than 15% on the 1 σ level". These estimates are based on tests of the procedure with known standards at different concentration levels described here. This estimate is further justified from the variability of the mixing ratios determined for long-lived compounds such as dichlorodifluoromethane at the coastal site, as the variations of the mixing ratios for these compounds are typical less than a few percent in rural and background air.

P2174 line 4: I recommend that the authors replace "paraffins" with "alkanes." Better to keep terminology consistent. We will follow the referees' recommendation.

P2174 line 21: Replace "felt" with "fell" We will follow this recommendation.

P2176 line 7: Yes, we meant our own unpublished data. This will be clarified.

P2181 lines 10-11: This remark is eligible. We will replace overall by analytical. According to the EURACHEM/CITAC Guide "Quantifying uncertainty in Analytical Measurements, 2nd edition 2000" in both cases repeatability is the more appropriate term. Therefore, we will replace overall reproducibility by analytical repeatability.

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 2161, 2011.